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# INVESTIGATIONS OF PHOTOCATALYTIC ACTIVITIES OF PHOTSENSITIVE SEMICONDUCTORS DISPERSED INTO EPOXY MATRIX

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## Abstract

New hybrid catalyst coating have been synthesised encapsulating TiO<sub>2</sub> nanoparticles into an epoxy matrix by means of UV-induced polymerization. It was shown that the presence of the titania nanoparticles did not significantly influenced the curing process. Morphological analysis of the achieved UV cured coatings containing titania showed an homogeneous distribution of the inorganic particles, with an average size between 130-160 nm. It is mandatory that the coating will not be itself degraded during UV irradiation. FT-IR measures performed on aged coatings subjected to UV irradiation for 41 days showed that the photodegradation of either the pristine epoxy coating or coating containing the photocatalyst were negligible.

The photocatalytic efficiency of these new catalysts was evaluated by studying the degradation of some organic compounds under UV light. Methylene blue was employed as model molecule to investigate the photoactivity toward organic molecule directly adsorbed on the coating surface. Under irradiation, complete dye degradation was achieved within 90 min. Phenol and 3,5-dichlorophenol were used as target molecules for studying photoactivity toward organic compounds dissolved in aqueous solution. Also in these cases, complete degradation of the organic compounds was achieved.

**Keywords:** TiO<sub>2</sub>, UV-curing, phenol, photocatalysis.

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## 1. INTRODUCTION

Heterogeneous photocatalysis represents an example of advanced oxidation processes (AOPs) capable of achieving a complete oxidation of organic and inorganic species [1-4]. It takes advantage of some semiconductor solids, which can be used as photocatalysts suspended in the water effluent to be treated, or immobilised on various types of supports. In the last few decades titanium dioxide has drawn much attention in the field of photocatalysis [5];  $\text{TiO}_2$  is the most preferred material thanks to its high photocatalytic activity, chemical/photocorrosion stability and non-toxicity [6]. It is well known that irradiation of  $\text{TiO}_2$  with an energy source higher than its band gap produces electrons and holes in the conduction band and valence band, respectively. These photo-generated holes and electrons can combine with the surface adsorbed species (e.g. water and oxygen) to form highly reactive radical species such as hydroxyl radical and superoxide anion [7]. These reactive species have strong oxidizing power and can complete mineralize most organic compounds, yielding carbon dioxide and dilute mineral acids as the final products [8,9].

Titania photocatalytic activity could be used in coatings applications in order to get self-cleaning surfaces which show photodegradation of organic pollutants adsorbed on the varnish surface. If titania will maintain its photocatalytic activity even when dispersed into a polymeric coating, this could be an interesting field of applications in coating industry.

For such, the UV curing technique was chosen because of its peculiarity and also because of its increasing importance in coatings applications; by UV irradiation it is possible to induce the polymer formation with a fast transformation of the liquid monomer into a solid film with tailored physical-chemical and mechanical properties. UV curing can be considered an environmental friendly technique, due to the solvent free process, and it is usually carried out at room temperature, therefore guarantees the saving of energy [10]. Furthermore, the cationic photopolymerization process of epoxy systems has some advantages compared to the radical one: lack of inhibition by oxygen, low shrinkage, good adhesion and mechanical properties of cured films[11].

The dispersion of photoactive titania into an organic polymeric coating is anyway a key issue to be solved in order to have a good dispersion of the ceramic filler within the polymeric network, maintain its photoactivity efficiency and protect the coating substrate from

degradation due to the strong oxidizing power of the TiO<sub>2</sub> photocatalyst. Different approaches have already been proposed in scientific literature and patents [12-14].

In a recent paper [15] we reported the photocatalytic study of a polysiloxane epoxy based UV cured coatings containing nano-TiO<sub>2</sub> in the anatase form. The selection of a polysiloxane resin was based on the fact that the main Si-O-Si chain is resistant to attack from TiO<sub>2</sub> photocatalysis, as was already previously reported in literature [16] and confirmed by our investigations.

By pursuing this research line we have investigated the photocatalytic effect of TiO<sub>2</sub> on organic molecules degradation. We have chosen as model compounds phenol, 3,5-dichlorophenol and methylene blue. Methylene blue (MB), a dye often used for catalytic tests [17,18], was chosen as target molecule to study reactivity on adsorbed phase. MB has been reported to be photo-bleached, demethylated and photodegraded under visible light when using a proper photocatalyst [19-23]. Phenol (P) and 3,5-dichlorophenol (3,5-DCP) were the target pollutants used to test the catalyst photoactivity in aqueous solution. In most studies P has been used as a molecule probe for photocatalytic tests, due to the fact that its degradation mechanism is well established [24-27]. The choice of 3,5-DCP as additional model molecule lies in the fact that: (a) it is a common and representative species of the class of chlorophenols in waters, (b) it is highly soluble in water relative to other polychlorinated phenols and (c) its simple molecular structure facilitates a greater understanding of the reaction mechanism involving aromatic compounds; moreover, additionally following of the chlorine atoms fate permits to ensure 3,5-DCP degradation.

## **2. EXPERIMENTAL**

### **2.1 Materials**

The 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate epoxy resin (**CE**) was purchased by Aldrich and used as epoxy based system. Triphenylsulfonium hexafluoroantimonate was used as photoinitiator, and it is commercially available from Aldrich in propylene carbonate solution at 50 wt.%.

Titanium dioxide was supplied by Degussa (TiO<sub>2</sub>, P25, Degussa, Germany, average particles size of 21 nm, specific surface area of 50 m<sup>2</sup>/g). Methylene blue, phenol and 3,5-dichlorophenol were all furnished by Aldrich and used as received.

### **2.2 Sample preparation**

For photocatalytic study on UV cured coating, the ceramic filler,  $\text{TiO}_2$  solution was added to the epoxy resin in order to prepare hybrid materials with a content in the range between 0.5 and 50 g/l with respect to the epoxy resin. The mixtures were stirred with Ultraturrax until a uniform dispersion was achieved. The cationic photoinitiator was added at 2 wt% in each formulations, coated on glass substrate and UV irradiated by means of Fusion lamp, with a light intensity on the surface of the sample of about  $500 \text{ mW/cm}^2$ . UV cured coatings of about  $100 \mu\text{m}$  were achieved.

The epoxy resin formulations containing  $\text{AgSbF}_6$  (1-5 wt%) and DMPA (2,2 dimethoxy-2-phenyl acetophenone 2 wt%) were coated onto glass substrates using a wire-wound applicator, and then the films were exposed to UV light under nitrogen atmosphere, with radiation intensity on the surface of the sample of  $30 \text{ mW/cm}^2$ , obtaining films of about  $100 \mu\text{m}$ . The obtained coatings were stained with an alcoholic solution of methylene blue (5 g/l of methylene blue in alcoholic solution) on the sample surface. Photocatalytic experiments were performed by irradiation with a medium pressure Hg arc lamp (Hamamatsu) equipped with an optical guide. The average light intensity on the reaction vessel at a distance of 15 cm from the lamp was found to be of around  $50 \text{ mW/cm}^2$ . The cured samples were analyzed by means of UV-Vis spectrophotometer following the methylene blue bleaching.

Phenol and 3,5-dichlorophenol were also used as target molecules to investigate the photocatalytic effect of the UV-cured material. Irradiation experiments were carried out in pyrex glass cells containing 40 ml of aqueous solution. Either the cured epoxy films containing 10 g/l of the semiconductor was dipped into a 30 mg/l phenol solution, or 200 mg/l of the semiconductor was dispersed into the 30 mg/l of phenol solution and again irradiated in the same conditions for comparison purpose. In all cases, experiments were run without modifying the natural pH of the solution. Experiment run on P had an initial pH of 6.8 and remains almost constant during the photocatalytic treatment. Experiments have been performed in air saturated conditions using a Blacklit Philips TLK/05 lamp ( $40 \text{ W/m}^2$ ) with the maxima emission at 360 nm. The temperature reached during the irradiation was  $38 \pm 2^\circ\text{C}$ . The entire content of the cells was then analyzed with the appropriate techniques.

### 2.3 Polymeric films characterizations

The kinetics of the photopolymerization were determined by Real-Time FT-IR spectroscopy, employing a Thermo-Nicolet 5700 instrument. The formulations were coated onto a silicon wafer. The sample was exposed simultaneously to the UV beam, which induces the polymerization, and to the IR beam, which analyzes *in-situ* the extent of the reaction. Epoxy

conversion was followed by monitoring the decrease in the absorbance of the epoxy ring centred at  $790\text{ cm}^{-1}$ . A medium pressure mercury lamp (Hamamatsu) equipped with an optical guide was used to induce the photopolymerization (light intensity on the surface of the sample of about  $30\text{ mW/cm}^2$ ).

The gel content was determined on the cured films by measuring the weight loss after 24 hours extraction with chloroform at room temperature, according to the standard test method ASTM D2765-84.

The morphology of the obtained materials was investigated by means of a Field Emission Scanning Electron Microscopy (FESEM, Supra 40 Zeiss). The surface fracture of the cured coatings were observed with the In-Lens detector. This detector is an ideal tool to investigate polymeric materials thanks to its high detection efficiency at very low acceleration voltages and the almost pure detection of SE electrons. The detector is placed above the objective lens and detects directly the beam path. The lower the energy of the primary electrons, the smaller the interaction volume and the penetration depth of the electrons will be. The smaller penetration depth of the electrons, the higher the share of SE electrons generated in the upper layers of the specimen, which contribute to the image contrast and resolution. This detector allows to collect images at very low acceleration voltages (1.5-5 kV) with the minimization and compensation of the effects due to the accumulation of local charges on the surface of non-conductive materials, that otherwise can significantly deteriorate the imaging quality.

The different alcoholic (absolute ethanol) powder suspensions, with solid content of 10 g/l, were prepared and maintained under magnetic stirring. The de-agglomeration degree of the dispersions was monitored by laser granulometry as a function of the stirring time up to achieve stable and well dispersed suspensions.

## **2.4. Samples analysis**

Methylene blue samples were analyzed by means of UV-Vis spectrophotometer following the dye bleaching. UV-Vis spectra were collected either on alcoholic solutions or on UV cured coatings by means of Perkin Elmer spectrophotometer.

The disappearance of phenol or 3,5-dichlorophenol as a function of the irradiation time was followed using an HPLC system (Merck-Hitachi L-6200 pumps), equipped with a Rheodyne injector, a RP C18 column (Lichrochart, Merck,  $12.5\text{ cm} \times 0.4\text{ cm}$ ,  $5\text{ }\mu\text{m}$  packing) and a UV-Vis detector (Merck Hitachi L-4200) fixed at 220 nm, using acetonitrile (40%) and phosphate buffer (60%,  $1 \times 10^{-2}\text{ M}$ ) at pH 2.8 as eluant at a flow rate of  $1\text{ ml/min}$ .

A Dionex instrument was employed for chloride analysis equipped with a conductimetric

detector using an AS9HC anionic column, 9 mM  $K_2CO_3$  as eluant and a flow rate of 1 mL/min. In these experimental conditions the retention time of chloride ion was 5.71 min.

### 3. RESULTS AND DISCUSSION

#### 3.1. Hybrid films preparation and characterization

After adding the ceramic powder into the epoxy resin, in the range between 0.5 and 2 g/l, the formulations were cured by means of UV light in the presence of a sulfonium salt as cationic photoinitiator.

The main concern on the use of the UV curing technique was the well known UV absorption property of anatase. It was therefore necessary to understand the possibility to cure by UV light formulations containing titania.

The conversion curves as a function of irradiation time for the pristine epoxy resin and in the presence of increasing amount of  $TiO_2$  are reported in Fig. 1.

When the  $TiO_2$  is added to the formulation, the rate of epoxy group conversion slightly decrease. The slight lowered rate of polymerization and epoxy group conversion may be due to the UV light shielding effect of  $TiO_2$  nanoparticles. This competitive effect of UV absorption with the photoinitiator will generate a lower amount of reactive species with a decrease of the epoxy group conversion. In any case, the shielding effect is really very limited because of the very low  $TiO_2$  content in the photocurable formulation. It is worth noting that the pristine epoxy resin did not reached 100 % of conversion because the samples vitrify, since the ultimate  $T_g$  of the materials is much above room temperature (around 180 °C, as determined by DSC analyses).

High gel content values (always above 98 %) were obtained for all UV cured coatings, indicating the formation of a highly cross-linked polymer network.

Morphological analysis of the achieved UV cured coatings containing titania was performed by FE-SEM analyses on the fracture surface of the cured films. In Fig. 2 the FE-SEM micrograph of the surface fracture for the epoxy coating containing 0.5 g/l of  $TiO_2$  is reported; an homogeneous distribution of the inorganic particles is evident with an average size between 130-160 nm.

This result shows a certain degree of particles agglomeration achieved during photocurable formulation preparation. This is a common phenomena due to the very high surface area of the ceramic filler which induces a strong tendency of agglomerations. Nevertheless, a good



dispersion and a relatively low degree of agglomeration was assured thanks to the high-mechanical dispersion of  $\text{TiO}_2$  into the liquid resin. The good dispersion and the low degree of agglomeration of the inorganic nanoparticles into the cured coatings is a key point for its catalytic activity, and this was maintained during UV-curing which occurred very rapidly and at room temperature, avoiding any extreme agglomeration phenomena which could be occurred if curing would have happened at high temperature (such as the epoxy hardening in the presence of amine performed at around  $100\text{ }^\circ\text{C}$ ). For this reason UV curing technique was a suitable epoxy-vulcanization method to be used in the preparation of these polymeric films containing ceramic nanoparticles.

To evaluate the photodegradation effect of the photocatalyst towards the cured epoxy substrate, the change of the IR spectra of the pristine epoxy network was compared with the change of the IR spectra of the coatings containing the  $\text{TiO}_2$  powders, under 41 day of UV irradiation (see Fig. 3).

In both cases an increase in the peak at  $3500\text{ cm}^{-1}$  was observed, due to moisture adsorbed by the coating. An increase of the peak centered at around  $1700\text{ cm}^{-1}$  could be attributed to the formation of ester groups, which could be attributed to a certain degree of degradation of the coatings. Nevertheless the peaks related to alkyl moieties remained practically unmodified ( $3000\text{--}2500\text{ cm}^{-1}$ ), so proving the coating stability toward UV irradiation. Furthermore the aged coatings did not showed any weakening and they did not showed weight decrease, which is a further evidence of the stability against aging of these coatings containing titania nanoparticles.

## **3.2 Photoactivity in adsorbed phase**

Methylene blue (see Fig. 4) was used as probe molecule to evaluate photoactivity of catalyst dispersed within epoxy material when dye is adsorbed on the UV-cured epoxy film. The coatings were stained with an alcoholic solution of methylene blue at a concentration of  $3\text{ g/l}$  and irradiated. The dye decomposition was evaluated by measuring the change in absorption for peak centred at  $650\text{ nm}$  in the UV-Vis spectrum of the stained coatings at regular interval of irradiation time.

### **3.2.1. Pristine film**

Direct photolysis experiments were preliminary run, with the aim of assessing if photolysis may contribute to the dye decomposition. When the dye is dispersed on the pristine film, MB has shown to be stable over the irradiation time interval considered and, within 2 hours of

irradiation, dye was only slightly degraded (approximately 10%, see disappearance curve plotted in Fig. 4).

### **3.2.2. Coating containing TiO<sub>2</sub>**

The UV cured coatings containing TiO<sub>2</sub> Degussa P25 were stained with an alcoholic solution of MB. Preliminary measurements were performed in the dark using coating with 0.5 gL<sup>-1</sup> TiO<sub>2</sub> content. Until 2h of contact, variation in dye concentration in the dark was negligible, as assessed by the UV-Vis spectra shown in Figure S1.

Under UV light the photocatalytic activity of the synthesized materials were evaluated as a function of the catalyst concentration. In Fig. 4 are shown MB degradation curves as a function of irradiation time for the epoxy coatings containing an increasing titania content, and, for comparison purpose, for MB degradation in aqueous solution in the presence of 0.5 gL<sup>-1</sup> dispersed TiO<sub>2</sub>; the rate constants calculated in the diverse experimental conditions are collected in Table 1. In the presence of aqueous MB solution containing dispersed TiO<sub>2</sub>, MB completely disappeared within 30 min, while with coated TiO<sub>2</sub> dye disappearance in absorbed phase occurs with an only slightly lowered rate and is completely abated within 2 h of irradiation. The initial increase in catalyst concentration leads to a slight enhance in the disappearance rate, while concentrations higher than 10 g/L showed a detrimental effect. The reduced photoactivity at high catalyst concentration could be attributable to the photonic efficiency level off at high catalyst concentration, when the increased light scattering reduces the photonic flux within the irradiated solution thus lowering the degradation rate [28, 29].

Finally, the dye was deposited on the same TiO<sub>2</sub>-based film (containing 20 g/L TiO<sub>2</sub>) for four times and irradiated; the calculated rate constants give a low standard deviation ( $0.040 \pm 0.001 \text{ min}^{-1}$ ), so showing that the coated film did not lose its photocatalytic property after use.

### **3.2.2. Coating containing TiO<sub>2</sub> /Ag**

Further studies were made with the purpose to increase the catalyst efficiency and to further approximate rate obtained with dispersed TiO<sub>2</sub>. It is well known that catalyst photoactivity can be reduced by direct recombination or by the presence of surficial defects that, together with the impurities presence on the catalyst surface, modify the electronic structure by introducing discrete levels in the band-gap. These levels cause a electron/hole pair recombination at lower energy or can act as electron trapping so hindering their migration [30]. An increased efficiency in charge separation may arise from coupling of Ag/TiO<sub>2</sub>, as

TiO<sub>2</sub> coupling with noble metals is known to reduce the extent of electron-hole pair recombination [31,32].

As already reported and discussed in previous papers [33,34], silver nanoparticles can be generated in-situ via a photo-reduction process, performed in the presence of AgSbF<sub>6</sub> and a radical photoinitiator. The electron donor alkoxybenzyl radicals formed from the photoinduced cleavage of 2,2-dimethoxy-2-phenyl acetophenone, are oxidized to the corresponding carbocations capable of initiating cationic cross-linking of the bis-epoxide, in the presence of silver hexafluoroantimonate with concomitant formation of silver nanoparticles. Therefore we could obtain cured epoxy network with titania nanoparticles which were added ex-situ and silver nanoparticles which were generated in-situ.

For such, we have prepared coatings by entrapping increasing amount of Ag in the material. Preliminary results obtained with this material are collected in Table 1; unfortunately, despite good dispersion of silver within the coating (see FE-SEM micrograph reported in Figure S2 in supplementary material) and the appearance of a new band in the UV spectra attributed to Ag (Figure S3 in supplementary material), rates are only scarcely modified by the Ag presence and the increase from 1 to 2% in Ag did not show a positive effect. Further studies on this material will be done in a near future.

### 3.2 Photo-activity in aqueous phase

The photoactivity of the prepared materials in aqueous solution was studied using phenol and 3,5-dichlorophenol as model molecules.

The photo-induced transformation of phenolic compounds was investigated as a function of the irradiation time in the presence of a coated catalyst and, for blank analysis, on pristine coating. Direct photolysis scarcely contribute to the phenol transformation; upon light exposure in pure water or with pristine coating degradation is negligible and after long irradiation times (14 days) only 15% of phenol was disappeared.

Phenol (P) and 3,5-dichlorophenol (3,5-DCP) are then irradiated with the synthesised photocatalysts and, for comparison purpose, with dispersed TiO<sub>2</sub>; Fig. 5 shows the case with TiO<sub>2</sub> at 0.5 g/L. P and 3,5-DCP followed similar degradation profiles (rates are respectively 0,029 h<sup>-1</sup> (phenol) and 0,027 h<sup>-1</sup> (3,5-dichlorophenol with coated TiO<sub>2</sub> or 0.84 (P) and 0.96 h<sup>-1</sup> (3,5-DCP) with dispersed TiO<sub>2</sub>) and the complete degradation was achieved within 48 h of irradiation. In aqueous solution the photoactivity of coated TiO<sub>2</sub> is drastically reduced, probably due to the difficulty for the organic compounds in reaching the surface active sites.

Together with the 3,5-DCP disappearance, chlorine was released in a stoichiometric amount as chloride ion within 48 h of irradiation. Chloride evolution follows a double kinetic, with the stoichiometric release of one of the two chlorine atom within 16 h, well-matched with the 3-CP formation described later, followed by the release of a second chlorine atom, kinetically reliable with 3-CP disappearance.

The UV cured coatings holding catalyst concentrations ranging from 0.5 to 10 g/L were tested on P degradation and the calculated rate constants are collected in Table 2.

When varying the catalyst concentration from 0.5 to 2 g/l, rates are scarcely influenced, while at higher catalyst concentration rate dramatically decreases. Again, this phenomenon is attributable to the photonic efficiency level off at high catalyst concentration, when the increased light scattering reduces the photonic flux within the irradiated solution thus lowering the degradation rate [28,29].

In a close analogy with what already done in adsorbed phase, the employ of Ag-doped coating was explored. Unfortunately, coating prepared by silver salts addition showed an even lowered rate (see Table 2).

### **3.3.2. Transformation products**

The formation of transformation products (TPs) was also monitored and compared with those coming from phenol transformation when using TiO<sub>2</sub> Degussa P25 dispersed in aqueous solution.

#### **3.3.2.1. Phenol TPs**

Phenol transformation in the presence of dispersed Degussa P25 is known to occur through the formation of hydroxyl derivative i.e. catechol (CAT), hydroquinone (HQ), 1,4-benzoquinone, resorcinol and, in a slight extent, of condensed products [7]. In our experimental conditions, the main intermediates were identified as hydroquinone (HQ) and catechol (CAT), while resorcinol (R) is detected at trace level. Their profiles as a function of irradiation times are shown in Fig. 6; in all cases, typical bell-shaped profiles are followed and, interesting, difference arose from their relative formation ratio when using dispersed TiO<sub>2</sub> (see Fig.6, top) and coated TiO<sub>2</sub> (see Fig. 6, middle and bottom). When employing dispersed TiO<sub>2</sub>, intermediates evolution strongly resembles that reported by Okamoto [35] under comparable conditions. Whereas the initial rates for catechol and hydroquinone formation on dispersed TiO<sub>2</sub> are comparable, relative ratio differs from that required for statistical reasons.

The ratio between CAT and HQ is 1:1.5, due to the strong adsorption of catechol on the catalyst surface [36-38], with formation of chelates with surficial OH groups [39,40].

Interesting, on coated TiO<sub>2</sub> the expectation namely the statistical 2:1 (CAT:HQ) ratio is fulfilled. On coated titania the maximum appeared concentration of catechol drastically increased, so implying that the polymeric material did not provoke specific surficial adsorption. This theory is confirmed by catechol adsorption studies made on coated TiO<sub>2</sub> where catechol recovery remains >99 % also after long dark equilibration time (72 h). The presence of epoxy group at the water/solid interface may hinder catechol adsorption/complexation at the catalyst surface; a partial shielding effect of the epoxy matrix toward surficial titanols should prompt phenol to mainly react with homogenous OH species rather than with adsorbed titanols, in a close analogy with what occurs on TiO<sub>2</sub>/F system [41]. When Ag salt are added the formation of catechol is further favoured and the ratio overcome that expected by statistical TPs distribution, due to a repressed hydroquinone formation.

#### **3.3.2.2. 3,5-Dichlorophenol TPs**

Dichlorophenols are known to degrade accordingly to an •OH radical mediated or e<sup>-</sup> mediated reaction [42]. 3,5-Dichlorophenol transformation is known to mainly proceed through the formation of 3-chlorophenol, phenol and dihydroxyderivatives.

In our experimental conditions, main identified TPs are 3-chlorophenol (3-CP), phenol (P) and catechol. TPs profile with dispersed or coated TiO<sub>2</sub> Degussa P25 are shown in Fig. 7. Again, even if the same TPs are formed with similar total concentration, their relative ratio is deeply modified when TiO<sub>2</sub> is encapsulated into the coating.

When analysing dispersed TiO<sub>2</sub>, 3,5-DCP transformation mainly proceeds through P formation (see Fig.7, top). In the presence of coated TiO<sub>2</sub>, 3-CP formation is enhanced while the phenol concentration is halved and the ratio 3-CP:P passes from 1:5 (TiO<sub>2</sub> solution) to 2:1 (coated TiO<sub>2</sub>). This trends is still maintained in the material doped with Ag (see Fig.7, bottom), where the reductive initial route seems even increased. 3-CP formation as key intermediate was already observed during the polichlorophenols reductive degradation [43,44] and involves an initial reductive attack. It is rather surprising that reductive pathways could be favoured when working with UV-cured materials and this phenomenon needs further investigation.

## **Conclusions**

In this paper the photocatalytic effect of titanium dioxide was evaluated dispersing the catalyst into an epoxy polymer network. The synthesised materials had shown an high activity on adsorbed phase, while in aqueous phase the degradation of organic compounds requires long irradiation time. The incorporation of the catalyst in the polymeric films through UV-curing technique then allows to achieve photodegradation of the organic molecules polluting the surface of polymeric coatings. This could find interesting applications in the field of varnishes in order to achieve self-cleaning painted surfaces, but it is mandatory that the coating will not be itself degraded during irradiation. FTIR measures prove that photodegradation rate of the pristine epoxy coating was negligible for an irradiation time of 984 hours, and comparable behavior was found for the photodegradation rate of the coating containing the photocatalyst. These results prove the advantage of dispersing the titania into a coating which could have photocatalytic activity but maintaining the good performance of the acrylic UV-cured coating.

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## Figure caption

**Figure 1:** Epoxy group conversion as a function of irradiation time for the pristine epoxy resin and for the resin filled with 500, 1000 and 2000 mg/l of TiO<sub>2</sub>.

**Figure 2:** FE-SEM micrograph of the surface fracture for the epoxy coating containing 0.5 g/L of TiO<sub>2</sub>

**Figure 3.** FT-IR spectrum of (top) pristine coating and (bottom) with dispersed TiO<sub>2</sub> after using a wheatearometer for 41 days: 0 min (blue line), 13 days (red line) and 41 days (green line).

**Figure 4:** Methylene blue degradation as a function of irradiation time in the presence of dispersed TiO<sub>2</sub> (D) or coating containing increasing TiO<sub>2</sub> concentrations.

**Figure 5:** Phenol and 3,5-dichlorophenol degradation as a function of irradiation time in the presence of 0.5 g/L dispersed TiO<sub>2</sub> (open symbols) or coated TiO<sub>2</sub> (full symbols).

**Figure 6:** Transformation products formed with dispersed (top) or coated (bottom) TiO<sub>2</sub>.

**Figure 7:** TPs formed from 3,5-dichlorophenol in the presence of dispersed (top), coated TiO<sub>2</sub> (middle) or coated TiO<sub>2</sub> /Ag (bottom)

Figure 1

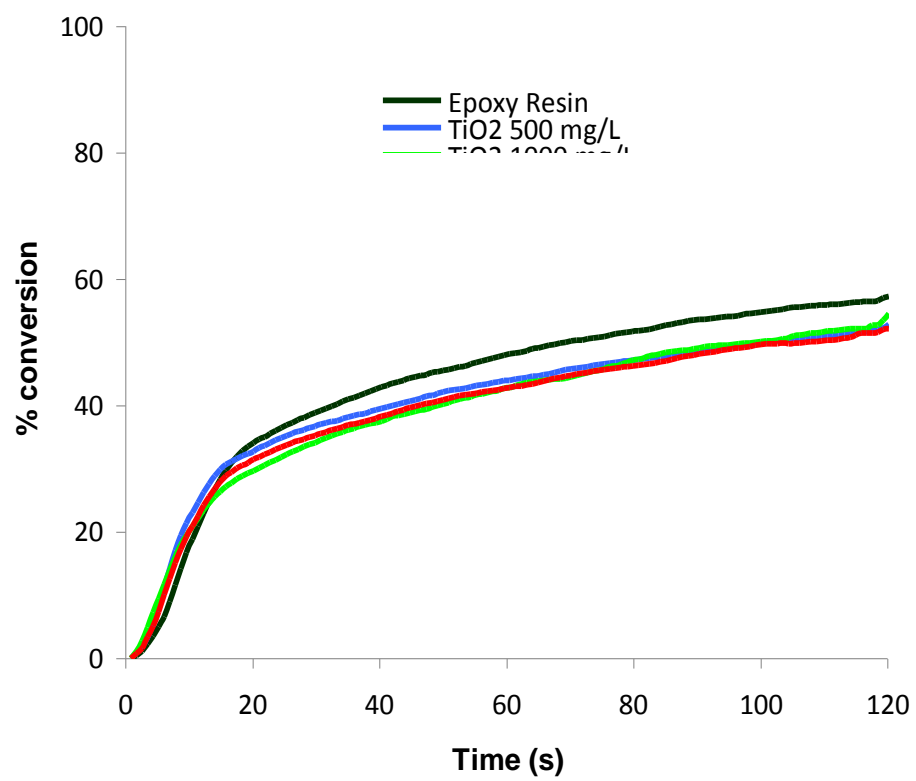


Figure 2

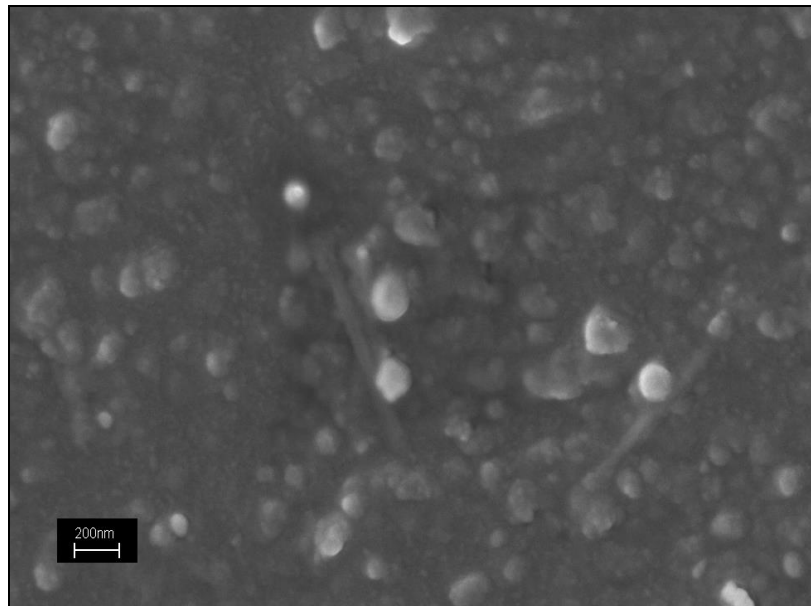


Figure 3

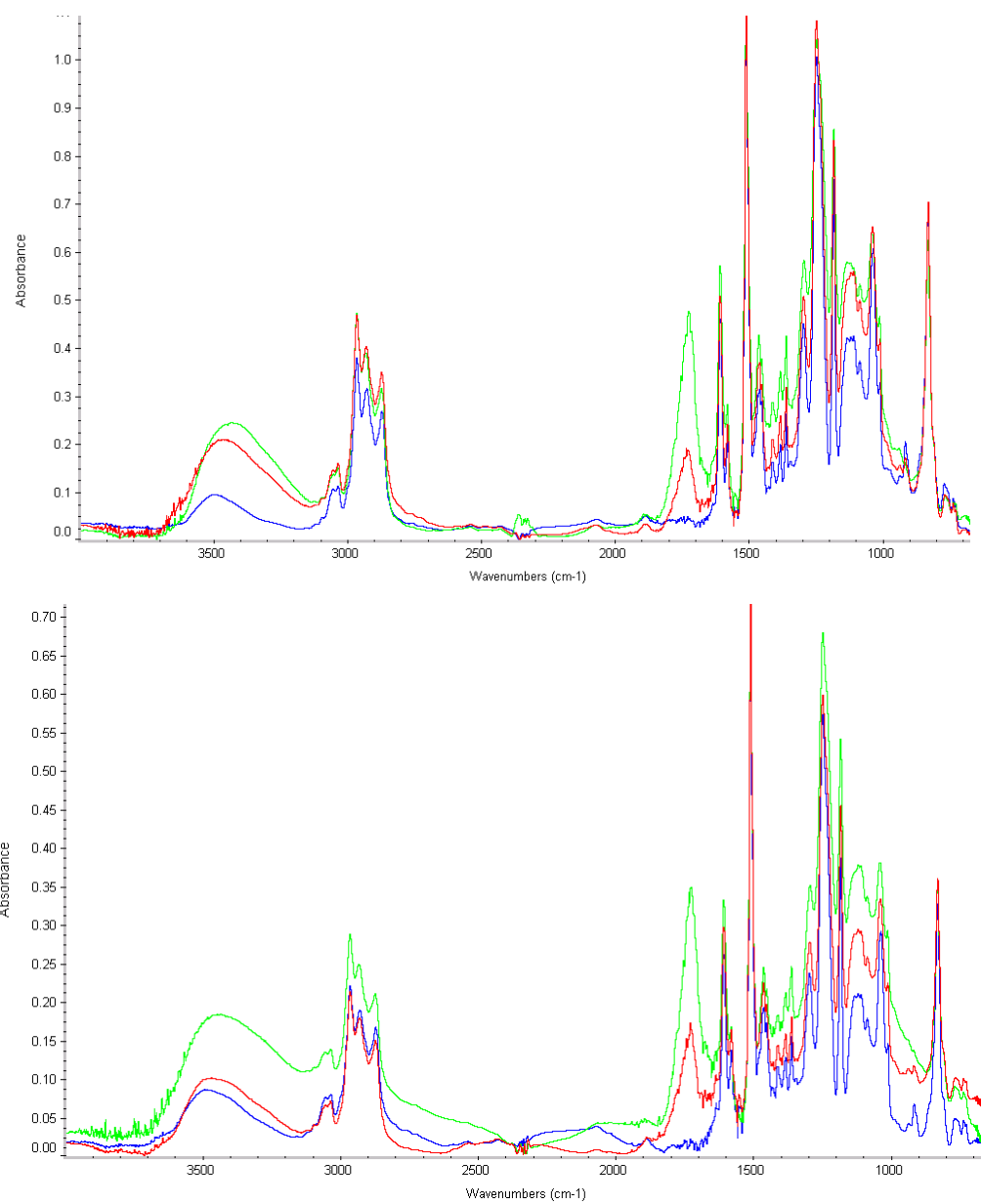


Figure 4

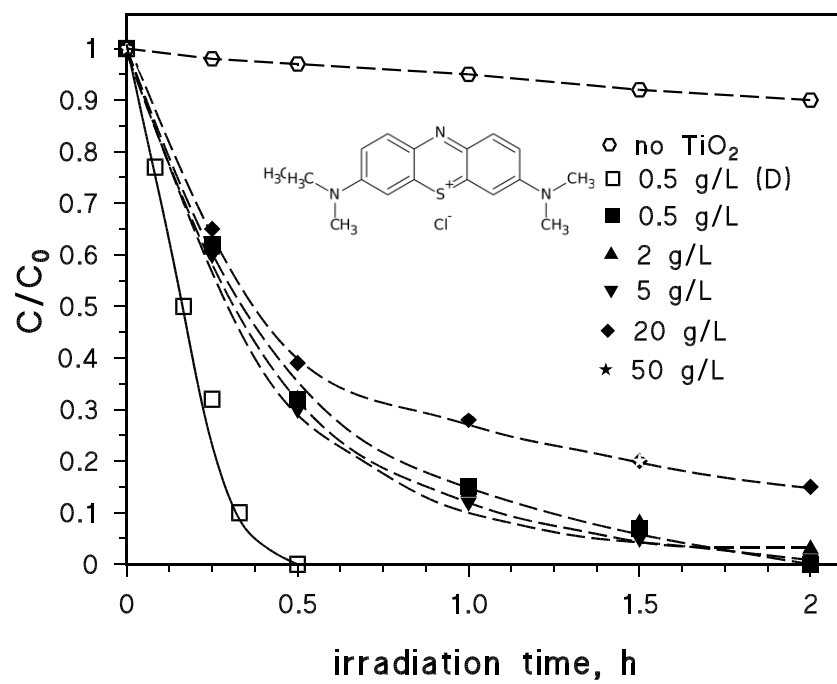


Figure 5

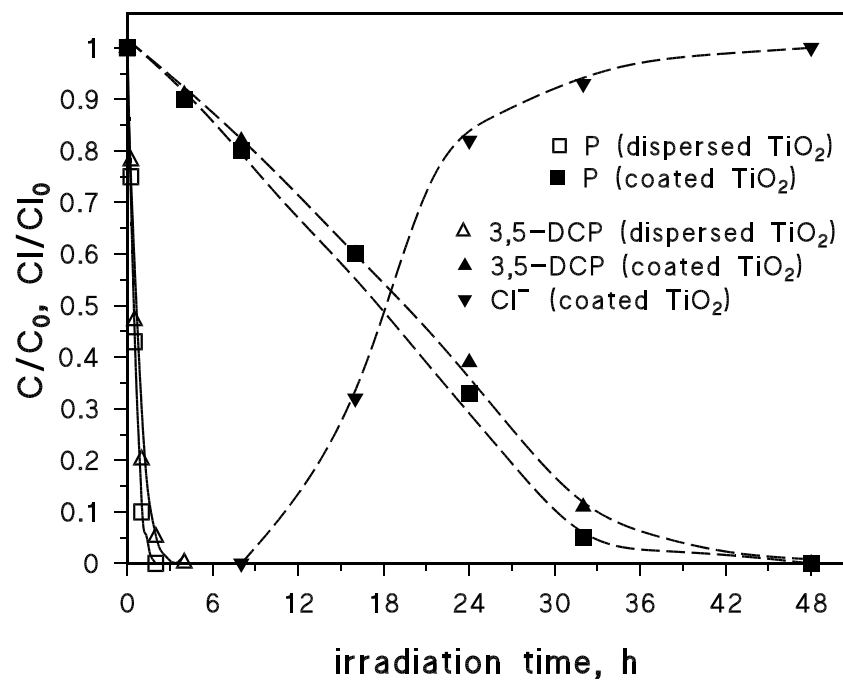


Figure 6

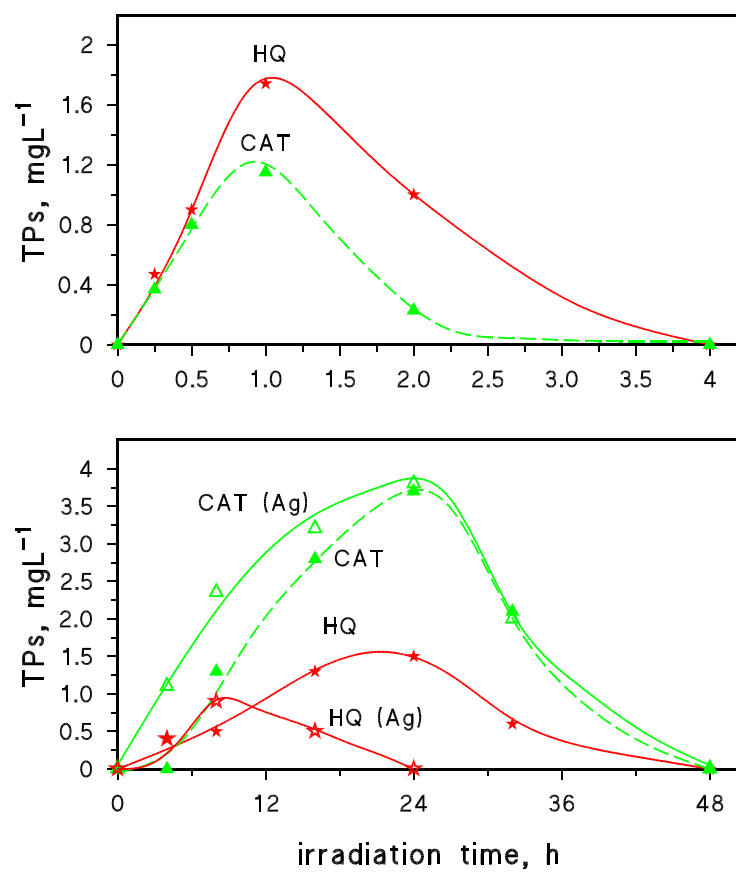
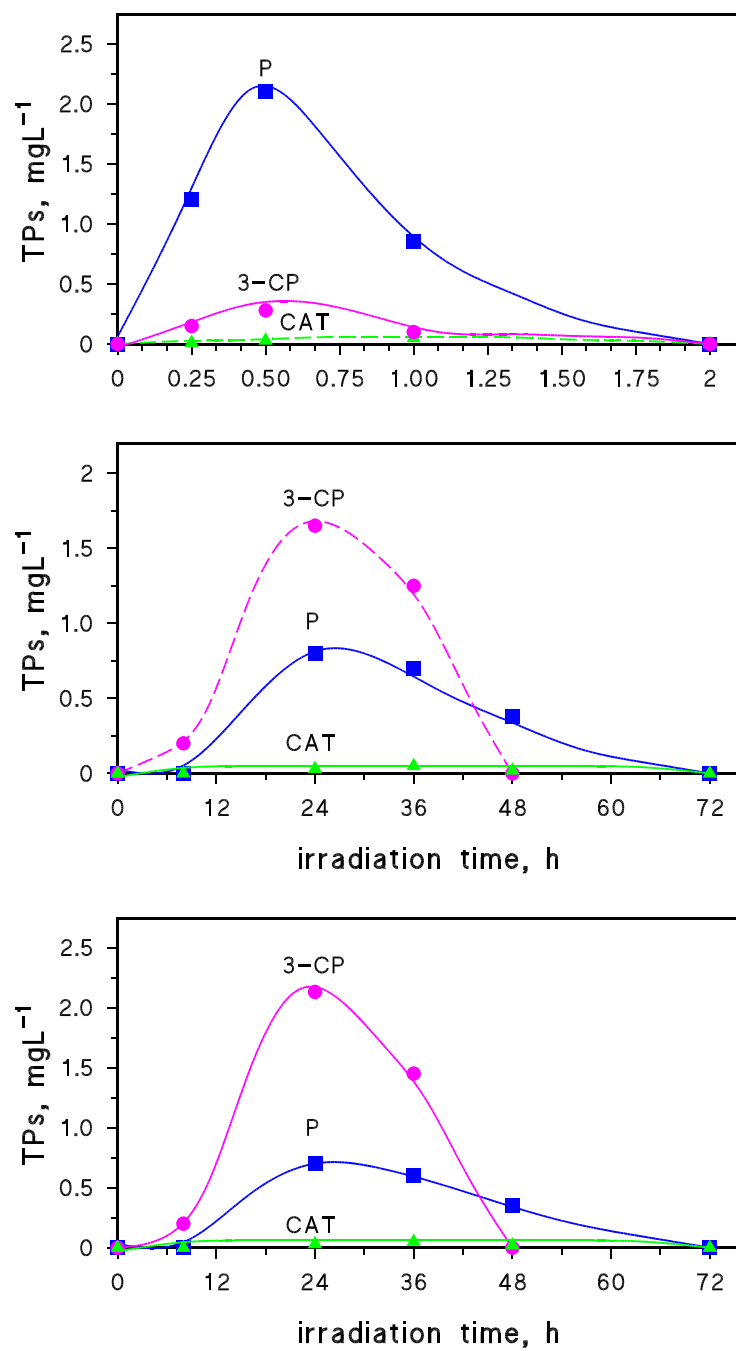


Figure 7





**Table 1.** Methylene Blue rate constants in adsorbed phase

TiO <sub>2</sub>			K [min <sup>-1</sup> ]
0.5 g/L	-		0,042
	Ag	1% w/w	0,030
		2% w/w	0,042
1 g/L			0,042
2 g/L			0,044
5 g/L			0,032
10 g/L			0,040
20 g/L			0,032
50 g/L			0,023

**Table 2:** Phenol rate constants in aqueous solution.

TiO <sub>2</sub>			K [h <sup>-1</sup> ]
0.5 g/L	-		0,029
	Ag	1% w/w	0,028
		2% w/w	0,029
1 g/L			0,028
2 g/L			0,028
10 g/L			0,0035